Optimization of management choices of clariflocculation process by means of qualitative multi-criteria analysis

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ABSTRACT

Every year ship traffic produces tons of liquid waste mainly consisting of bilge water and of washing water of tankers' tanks. The latter are called slop waters and are characterized by high salinity and by the presence of recalcitrant pollutants mainly of hydrocarbon origin: these characteristics promote the use of chemical-physical rather than biological treatment. In particular, in the present study the slop waters were subjected to a clariflocculation treatment by means of batch tests. This treatment involves the dosage of specific chemical reagents (coagulants and flocculants) added to water at different stages of the process. In order to establish the optimal reagents' type and dose, also considering the operating costs, the proposed study presents a frequency analysis belonging to the family of multi-criteria exploration. The application of this methodology to examine the validity of the different process alternatives has allowed the inclusion of, in a single assessment, both economic and extra-economic (measurable only in qualitative terms) procedures. Thanks to this qualitative and quantitative method, it was therefore possible to order the different treatment alternatives analyzed, identifying the one that allows optimizing the wastewater management, for a conscious choice of the most suitable solution to the problem.

Key words | clariflocculation, frequency analysis, jar test, multi-criteria analysis, slop waters

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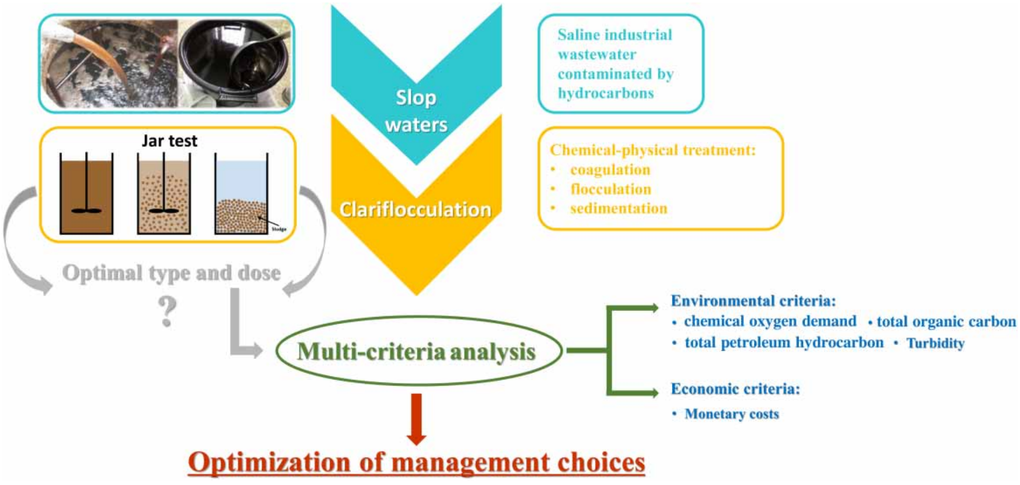
HIGHLIGHTS

- Clariflocculation is a chemical-physical treatment allowing removal of the main pollutants of saline industrial wastewater contaminated by hydrocarbons.
- The multi-criteria analysis allows optimization of the wastewater treatment management guiding in the choice of the type and dose of reagents to be used.
- The methodology enables a joint analysis of the environmental and economic impact of the evaluated process, allowing a more complete answer on the best option among the possible alternatives.
- From the application of the analysis, it emerged that, for this type of water, aluminum sulfate is a preferable coagulating agent over ferric chloride and that the optimal dose is equal to 90 mg L^{-1}.
- The addition of the flocculating agent results in a limited improvement in the treatment efficiency against an excessive increase in costs.

doi: 10.2166/wst.2020.186

GRAPHICAL ABSTRACT



INTRODUCTION

According to the United Nations organization, maritime pollution consists of direct or indirect introduction into the marine environment of substances able to produce negative effects on biological resources, human health, maritime activities, and water quality (GESAMP 1991). Nowadays, the spill from ships of liquid waste contaminated by hydrocarbons is one of the main causes of marine pollution. These spills can be accidental, i.e., due to accidents at sea, or systematic and therefore linked to the normal operations of discharging of bilge water or washing water from tankers' tanks (slop waters). The treatment of such waste, characterized by high hydrocarbon concentrations, high salinity, and by the presence of oils, represents a serious problem worldwide due to the persistence and accumulation of xenobiotic compounds in the environment (IMO – MARPOL 73/78).

It is not easy to identify a single treatment process that can completely remove all the forms of oil mixed with water and other pollutants (Abdel-Shafy *et al.* 2020). Slops can be treated using a biological process that, however, must be preceded by a chemical and/or physical pre-treatment (Ribera-Pi *et al.* 2020). This is because in the literature several problems related to the sedimentation of biological mud in saline environments are known (Woolard & Irvine 1995). Among the causes of this phenomenon is the greater density of salt water compared with fresh water: this generates buoyancy thrusts that resist the gravimetric decantation of the sludge. Secondly, the high salinity in wastewater causes a considerable increase in the osmotic pressure between the liquid bulk and the intracellular content: this implies a strong concentration gradient between what is contained within the cellular membranes of microorganisms and the mixed liquor (Kargi & Dincer 1997).

Generally, after the oil separation from these waters, the slops are subjected to a chemical-physical process to remove the pollutants present. Specifically, among the applicable treatments, clariflocculation shows a high removal efficiency of various pollutants (Bruno *et al.* 2020). The pollutants considered in this study are chemical oxygen demand (COD), total organic carbon (TOC), total petroleum hydrocarbon (TPH), and suspended solids.

Clariflocculation is a treatment consisting of the combination of three processes: coagulation, flocculation, and sedimentation. Coagulation is a rapid and intense mixing phase in order to destabilize colloidal suspensions (the main cause of turbidity) by adding coagulants that reduce the area of influence between the particles. In this way, the electric potentials present on the surface of the particles diminish and the attractive forces tend to prevail over the repulsive ones, allowing the suspensions to interact with each other and aggregate into micro-flakes. The process generally involves the use of iron or aluminum salts ($Al_2(SO_4)_3$, $AlCl_3$, $FeCl_3$, $Fe_2(SO_4)_3$, $FeSO_4$). The choice of the type and dose of the coagulant is not immediate since it depends on several factors: the pH, the agitation speed during the coagulation phase, the origin of the sample itself (Guida *et al.* 2007). Furthermore, the same coagulant may be adequate for the removal of certain pollutants but insufficient to remove others. The coagulant can also lead to an excessive production of sludge, determining the problem of their correct disposal (Aragonés-Beltrán *et al.* 2009).

The subsequent flocculation phase consists of the slow and constant mixing of the wastewater, allowing the agglomeration of the previously destabilized particles that form flakes of gradually increasing dimensions. In this case is again possible to resort to chemical agents (flocculants) that improve efficiency, influencing above all the speed of flake formation, the characteristics of the flakes (size and specific weight), and the consequent sedimentation speed in the last phase of the process (Mhaisalkar *et al.* 1991).

Decisions on water quality management have significant consequences on both the environment and the economic and social conditions of the area (Zarghami & Szidarovszky 2011; Alamanos *et al.* 2018).

Water quality management is a typical example for environmental decision-making that has to deal with multiple objectives, many different alternatives, several criteria, and large uncertainties in the prediction of their consequences. For water quality management decisions, it is important to be informed about the changes in substance concentrations that can be expected from different management alternatives (Schuwirth *et al.* 2018). The purpose or ultimate goal of a multi-criteria decision-making method is to investigate a number of alternatives in the light of multiple criteria and conflicting objectives (Voogd 1982). The environmental, social, and economic impacts derived from treated wastewater are an intrinsically complex multidimensional process that involves multiple criteria and multiple stakeholders (Gómez-López *et al.* 2009).

Multi-criteria analysis techniques have been successfully implemented in water quality management. In literature, several studies on the application of multi-criteria analysis methods to water quality management help stakeholders to make decisions (Hamed 2019).

Schuwirth *et al.* (2018) evaluate 10 different water quality management alternatives that tackle macro and micropollutants from a wide spectrum of agricultural and urban sources. They evaluate costs and water quality effects of the alternatives under four different socioeconomic scenarios (Schuwirth *et al.* 2018).

Hadipour *et al.* (2016) applied the analytical hierarchy process method to find the best alternative for using wastewater in Iran. Results show that groundwater recharge is the best alternative for wastewater reuse, followed by environmental use. They suggest this approach to help decision makers through giving solutions to manage water resources (Hadipour *et al.* 2016).

Gómez-López *et al.* (2009) applied the TOPSIS method to six different methodologies concerning the disinfection of treated wastewater before reuse. Results have shown that the best disinfection technique for treated wastewater has been chlorination for an urban, agricultural, or industrial use, while in recreational and environmental uses, the alternative of ultraviolet light disinfection was the chosen alternative (Gómez-López *et al.* 2009).

The main objective of the research is to determine the optimal parameters (in terms of type and dose of coagulant and flocculant) of the clariflocculation processes for the elimination of pollutants in saline wastewater contaminated by hydrocarbons. The scientific goal is achieved through the application of the frequency analysis method belonging to the family of multi-criteria analyses by first favoring an environmental scenario and then an economic one. Taking into account an environmental and an economic scenario, 36 design alternatives are compared by means of jar tests.

This analysis allows addressing complex problems by evaluating all the variables individually, but in an integrated way, attributing to each of them its relative importance. This allows examination of the problem from multiple points of view at the same time, thus also from an economic, social, and environmental one as required by the idea of intervention sustainability (Boggia 2007).

Frequency analysis is one of the multi-criteria evaluation methods that is easy to apply even for the non-experts. This method allows you to review the decision-making process in order to allow the participation of the public in the formation of the rankings of merit for the different plans or projects proposed (Bazzani & Malagoli 1993).

METHODS

Characterization of wastewater (or introduction of case study)

The slop waters deriving from the washing of oil tankers containing mainly diesel fuel, as already mentioned, consist of heavy hydrocarbons and other impurities generated by the residues of petroleum product mixed with seawater. In order to reduce the high content of suspended oils, a preliminary separation was initially carried out by simple gravity: the oils present, having a specific weight generally lower than that of water, tend to float on the surface and from here they can be removed. As shown in Table 1, in which all the wastewater characteristics after oil removal are reported, the organic matter in terms of COD and TPH are the main polluting

Table 1 | Characteristics of slop waters after oil removal and legislative limits imposed by Legislative Decree 152/2006

Parameter	Symbol	Value	Legislative limit (Lgs.D. 152/2006)	Units
Chemical oxygen demand	COD	1088 ± 251	≤160	mg L^{-1}
Total petroleum hydrocarbon	TPH	232.5 ± 28.5	≤5	mg L^{-1}
Total organic carbon	TOC	19.1 ± 3.3		mg L^{-1}
Total carbon	TC	57.4 ± 4.6		mg L^{-1}
Inorganic carbon	IC	38.2 ± 4.82		mg L^{-1}
Turbidity		25 ± 5.4		
Suspended solids	SS	352.4 ± 84.1	≤80	mg L^{-1}
Aluminum	Al	<0.005	≤1	mg L^{-1}
Arsenic	As	<0.001	≤0.5	mg L^{-1}
Boron	Bo	5.02	≤2	mg L^{-1}
Cadmium	Cd	<0.001	≤0.002	mg L^{-1}
Chrome	Cr	<0.005	≤2	mg L^{-1}
Iron	Fe	1.18	≤2	mg L^{-1}
Manganese	Mn	<0.005	≤2	mg L^{-1}
Nickel	Ni	<0.005	≤2	mg L^{-1}
Copper	Cu	<0.005	≤0.1	mg L^{-1}
Selenium	Se	<0.005	≤0.03	mg L^{-1}
Lead	Pb	<0.005	≤0.2	mg L^{-1}
Zinc	Zn	<0.005	≤0.5	mg L^{-1}
Chloride	Cl	8277 ± 121	≤1200	mg L^{-1}
Conductivity		48.4 ± 26.5		mS cm^{-1}
pH		7.78 ± 0.62	5.5–9.5	

components of the wastewater. In fact, the preliminary phase of oil separation considerably reduces turbidity. Concerning the presence of heavy metals in the wastewater, the data show that there is only a low concentration of iron and boron. However, these metals do not represent pollutants of interest. Finally, the chloride concentration and conductivity are high if compared with conventional wastewater.

Jar test

The present experimental study is specifically concerned with the treatment of slop waters coming from tankers used to transport oil products operating in the port of Augusta, Syracuse. For the treatment of these particular industrial wastewaters by the clariflocculation process, a jar-test apparatus was used. This device is equipped with vertical stirrers rotating at different speeds during the different phases of the process. Specifically, at the beginning the mixer rotated at a speed of 200 rpm for 1 minute to make coagulation possible; subsequently, to allow the flocculation, a speed of 30 rpm was set for a time of 20 minutes. Finally, after coagulation and flocculation phases, the suspension was poured into graduated cylinders for the sedimentation phase and subsequent measurement of the residual pollutants on the supernatant produced after two hours. To identify the appropriate type and dose of coagulant, two different trivalent salts were used in the coagulation phase: aluminum sulfate $Al_2(SO_4)_3$ and ferric chloride $FeCl_3$ in dosages between 50 and 90 mg L^{-1}. In the following flocculation phase, the anionic polyelectrolyte Polidal A57 was added as a flocculant in doses ranging from 1 to 10 mg L^{-1}, in order to evaluate the optimal one. Table 2 shows the codes of the various performed tests.

Multi-criteria decision analysis methods

Multi-criteria analysis or multi-criteria decision analysis (MCDA) has seen an incredible amount of use over the last several decades (Velasquez & Hester 2013). As known, MCDA is a process able to guide the decision makers to choose the most appropriate solution. It is useful when

Table 2 | Identification codes of the jar tests performed with different types and doses of coagulants and flocculant

$FeCl_3 + A57$			$Al_2(SO_4)_3 + A57$		
Test code	**Coagulant dose [mg L^{-1}]**	**Flocculant dose [mg L^{-1}]**	**Test code**	**Coagulant dose [mg L^{-1}]**	**Flocculant dose [mg L^{-1}]**
FCL_{50}	50	–	ALS_{50}	50	–
$FCL_{50}A57_1$	50	1	$ALS_{50} + A57_1$	50	1
$FCL_{50}A57_{2.5}$	50	2.5	$ALS_{50} + A57_{2.5}$	50	2.5
$FCL_{50}A57_5$	50	5	$ALS_{50} + A57_5$	50	5
$FCL_{50}A57_{7.5}$	50	7.5	$ALS_{50} + A57_{7.5}$	50	7.5
$FCL_{50}A57_{10}$	50	10	$ALS_{50} + A57_{10}$	50	10
FCL_{70}	70	–	ALS_{70}	70	–
$FCL_{70}A57_1$	70	1	$ALS_{70} + A57_1$	70	1
$FCL_{70}A57_{2.5}$	70	2.5	$ALS_{70} + A57_{2.5}$	70	2.5
$FCL_{70}A57_5$	70	5	$ALS_{70} + A57_5$	70	5
$FCL_{70}A57_{7.5}$	70	7.5	$ALS_{70} + A57_{7.5}$	70	7.5
$FCL_{70}A57_{10}$	70	10	$ALS_{70} + A57_{10}$	70	10
FCL_{90}	90	–	ALS_{90}	90	–
$FCL_{90}A57_1$	90	1	$ALS_{90} + A57_1$	90	1
$FCL_{90}A57_{2.5}$	90	2.5	$ALS_{90} + A57_{2.5}$	90	2.5
$FCL_{90}A57_5$	90	5	$ALS_{90} + A57_5$	90	5
$FCL_{90}A57_{7.5}$	90	7.5	$ALS_{90} + A57_{7.5}$	90	7.5
$FCL_{90}A57_{10}$	90	10	$ALS_{90} + A57_{10}$	90	10

several often conflicting points of view must be taken into consideration. Multi-criteria methodologies allow the acceptance of a project or the formulation of a ranking of projects examined through the comparison of the behavior of each of them with respect to environmental aspects. They are based on the criterion of 'technical efficiency' by Pareto. Any solution is deemed efficient when it is impossible to move to another solution which would improve at least one criterion and make no criterion worse (Zopounidis & Pardalos 2010).

The selection of the most appropriate technique depends on several factors, among others the nature and characteristics of the problem, the scope of the decision-making process, and other factors, such as the ease of handling each approach and the type of information required (Demirel *et al.* 2018).

In general, the main methodologies can be divided into:

- monetary methodologies
- non-monetary methodologies
- descriptive methodologies.

Non-monetary methodologies are used for environmental impact assessments. In fact, it is not easy to assess the external effects of a given project in monetary terms, as the goods and services involved are often immeasurable and intangible.

The main multidimensional methodologies adopted in the environmental impact assessment are divided into quantitative and qualitative methodologies (Wątróbski *et al.* 2019) (Figure 1).

They differ mainly in the type of information they need. The first group includes models whose information is defined as 'hard'. Environmental aspects are difficult to classify. The second group includes models whose information is defined as 'soft'. These models have effects that are not unambiguously interpreted.

Quantitative multi-criteria methodologies may be applied where the available information is of a cardinal nature.

When this method is not possible, for example in the context of cultural-architectural, environmental-recreational, historical-social evaluations, the approach becomes qualitative. In this case the evaluation is determined by judgments expressed on an ordinal scale.

Qualitative multi-criteria methodologies: frequency analysis

As mentioned above, the frequency analysis, as other qualitative methods, is based on the lack of attribution of numerical values during the different evaluation phases.

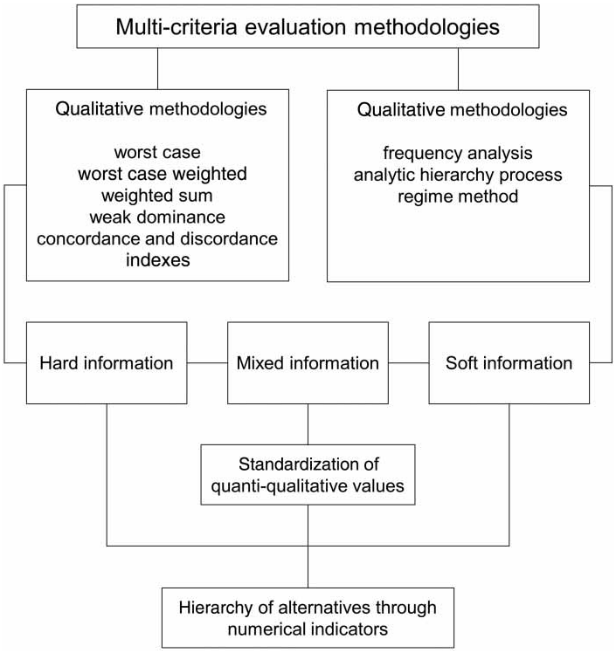


Figure 1 | Main multidimensional methodologies adopted in the environmental impact assessment (Bazzani & Malagoli 1993).

The method develops in:

(1) identification of treatment alternatives;
(2) definition of the evaluation criteria;
(3) definition of the indicators of the evaluation criteria;
(4) definition of the impacts of projects on individual evaluation criteria;
(5) construction of the evaluation matrix;
(6) construction of the frequency table;
(7) evaluation of alternatives on the basis of the performance of the selected criteria.

The study was carried out by identifying 36 treatment alternatives with different types and doses of coagulants and flocculants. The coagulants chosen are aluminum sulfate $Al_2(SO_4)_3$ and ferric chloride $FeCl_3$ (dose 50, 70, and 90 mg L^{-1}), while the flocculant chosen is the anionic polyelectrolyte Polidal A57 (dose 1, 2.5, 5, 7.5, and 10 mg L^{-1}). The choice of the type of chemical reagents derives from careful bibliographic research carried out on studies concerning the treatments generally used for this type of wastewater. In the same way, the doses investigated fall within a typical range for the clariflocculation treatment applied to industrial wastewater.

The selection criteria are the parameters generally used to evaluate the removal efficiency of wastewater treatments: COD, TOC, TPH, and turbidity. The environmental indicators are removal efficiency and total cost.

In order to rank the different alternatives, four levels of impact (++++, +++, ++, +) and three levels of weight (***, **, *) are defined, taking into account the distinction between 'treatment' and 'pretreatment'. This tool allowed comparison of the data favoring first an environmental scenario and then an economic one. The results led to a valid management compromise between the two aspects mentioned.

A first rather important phase of the evaluation procedure consists of defining the relevant selection criteria and environmental indicators.

'Evaluation criteria' are defined as the execution of a plan or project whose purpose is to achieve a given objective. In this work, the 'criterion' represents the objective to reach through the different types of treatment relating to the management of the clariflocculation process, i.e., the best chemical reagent and the best dose to use in the treatment. In particular, objectives of the evaluation are the removal capacities (in terms of performance) of the main pollutants usually considered for this type of waste, namely COD, TPH, TOC, and turbidity. As a further criterion, the total cost of the coagulants and of the flocculant, as well as the cost of the various reagents related to the pH change, was identified: hydrochloric acid (HCL) and sodium hydroxide (NaOH), deduced by referring to the technical sheets of various companies operating in the sector. To order hierarchically the different design alternatives, the present study defines the impacts that the different reagents used

Table 3 | Impact assessment indexes

Index	Impact
++++	Optimum
+++	Satisfactory
++	Mediocre
+	Very bad

Table 4 | Preferability attributed to the criteria

Symbol	Preferability
***	High
**	Medium
*	Low

Table 5 | Removal yields in the different jar tests

	ηCOD		ηTC		ηTOC		ηTurbidity		ηTPH	
Test code	**%**	**SD**	**%**	**SD**	**%**	**SD**	**%**	**SD**	**%**	**SD**
FCL$_{50}$	20.60	6.1	38.55	5.5	71.32	3.5	40.30	12.5	43.62	6.0
FCL$_{50}$A57$_{1}$	21.15	6.0	42.00	5.2	71.39	3.5	37.97	12.6	47.22	5.7
FCL$_{50}$A57$_{2.5}$	21.97	6.0	43.10	5.1	67.39	4.0	48.00	12.0	63.66	3.9
FCL$_{50}$A57$_{5}$	22.89	5.9	43.29	5.1	65.99	4.2	82.36	3.2	64.12	3.8
FCL$_{50}$A57$_{7.5}$	22.99	6.4	44.02	5.0	57.27	5.3	89.83	2.2	64.40	3.8
FCL$_{50}$A57$_{10}$	23.08	7.2	45.78	4.9	52.86	5.8	88.86	2.4	65.50	3.7
ALS$_{50}$	50.28	2.9	29.19	4.0	64.56	4.3	72.30	3.7	29.70	6.3
ALS$_{50}$ + A57$_{1}$	57.72	5.3	29.02	4.2	71.30	3.5	71.65	4.0	28.38	6.4
ALS$_{50}$ + A57$_{2.5}$	66.09	7.4	28.49	3.9	77.33	2.8	62.58	5.1	26.30	6.6
ALS$_{50}$ + A57$_{5}$	68.75	6.0	27.08	4.2	73.14	3.3	74.02	3.4	41.81	5.2
ALS$_{50}$ + A57$_{7.5}$	70.59	5.6	25.64	4.0	67.12	4.0	79.23	2.9	38.36	5.5
ALS$_{50}$ + A57$_{10}$	81.90	6.5	24.42	4.0	64.26	4.4	79.64	2.9	24.14	6.8
FCL$_{70}$	20.96	4.5	41.05	5.3	65.20	4.3	65.72	7.6	44.04	6.0
FCL$_{70}$A57$_{1}$	21.79	3.6	52.63	4.3	84.18	1.9	60.64	8.5	47.92	5.6
FCL$_{70}$A57$_{2.5}$	21.79	3.9	53.78	4.2	81.50	2.3	69.40	7.5	61.38	4.1
FCL$_{70}$A57$_{5}$	21.97	4.1	58.38	3.8	81.85	2.2	82.48	3.8	64.70	3.8
FCL$_{70}$A57$_{7.5}$	22.34	4.1	58.98	3.7	86.07	1.7	83.14	4.2	65.63	3.7
FCL$_{70}$A57$_{10}$	22.43	4.1	59.56	3.7	86.64	1.6	84.36	3.5	67.56	3.5
ALS$_{70}$	63.61	3.2	26.46	5.8	48.00	6.4	74.36	2.8	48.49	4.6
ALS$_{70}$ + A57$_{1}$	65.63	2.6	26.21	5.6	51.50	6.0	75.20	2.9	67.24	2.9
ALS$_{70}$ + A57$_{2.5}$	65.72	2.4	26.73	7.1	55.99	5.4	76.96	2.7	56.03	3.9
ALS$_{70}$ + A57$_{5}$	68.48	2.1	27.73	7.1	52.69	5.8	80.28	2.0	53.69	4.1
ALS$_{70}$ + A57$_{7.5}$	77.12	4.9	23.96	8.4	49.04	6.3	80.92	1.8	54.74	4.0
ALS$_{70}$ + A57$_{10}$	84.01	2.4	22.67	7.5	45.11	6.7	83.48	1.6	60.78	3.5
FCL$_{90}$	21.42	3.4	47.44	4.7	60.97	4.8	79.04	1.9	44.31	6.0
FCL$_{90}$A57$_{1}$	22.07	3.2	53.62	4.2	63.57	4.5	76.40	2.1	49.48	5.4
FCL$_{90}$A57$_{2.5}$	22.07	3.4	53.62	4.2	65.10	4.3	67.72	4.8	51.47	5.2
FCL$_{90}$A57$_{5}$	22.16	3.7	52.09	4.3	62.02	4.7	77.72	2.1	60.43	4.2
FCL$_{90}$A57$_{7.5}$	22.62	3.6	50.37	4.5	59.11	5.0	75.52	2.3	63.92	3.9
FCL$_{90}$A57$_{10}$	23.08	3.7	49.02	4.6	55.27	5.5	81.68	1.7	70.69	3.1
ALS$_{90}$	58.85	5.4	32.73	5.9	72.71	3.3	77.08	1.2	47.78	4.7
ALS$_{90}$ + A57$_{1}$	72.57	4.3	34.87	6.3	69.63	3.7	83.20	0.7	38.79	5.5
ALS$_{90}$ + A57$_{2.5}$	77.73	6.2	41.16	6.2	77.31	2.8	87.60	0.3	40.52	5.3
ALS$_{90}$ + A57$_{5}$	84.00	8.6	42.92	6.7	65.19	4.3	86.80	0.7	41.26	5.2
ALS$_{90}$ + A57$_{7.5}$	79.76	4.4	49.69	5.9	53.32	5.7	94.72	0.4	41.55	5.2
ALS$_{90}$ + A57$_{10}$	72.57	4.8	46.60	6.0	48.35	6.3	92.96	0.6	43.00	5.1

have on the individual criteria analyzed. According to the limits imposed by Legislative Decree 152/06, four different indexes have been carefully imposed to express the impacts on the different evaluation criteria (Table 3).

In a similar way, the priorities (i.e., the weights) of the criteria, expressed on an ordinal scale, must be made explicit, taking into account the importance according to distinct preferences (Table 4).

RESULTS AND DISCUSSION

In order to identify the best coagulant and flocculant dose, the removal performance of the different contaminants after the specific jar tests have been calculated in terms of percentage of pollutant removal from raw water (slops), according to Equation (1):

$$\eta_x = \frac{x_{\text{slop}} - x_{\text{treated}}}{x_{\text{slop}}} \cdot 100\ [\%] \qquad (1)$$

where x_{slop} and x_{treated} respectively represent the concentrations of the pollutant (COD, total carbon (TC), TOC, TPH, turbidity) before and after treatment. Table 5 summarizes the removal yields obtained in the various jar tests and the standard deviations from the average value, since the data refer to the average value obtained after a certain number of replicates (usually 3), performed with a variable pH in the range 6.5–7.5.

At this point, the study evaluated the impacts considering two different process scenarios: (i) clariflocculation as treatment and (ii) clariflocculation as pretreatment. In fact, the law imposes quite different removal limits depending on the function of the treatment within the entire chain. When the clariflocculation is used as the main treatment, the pollutant removal yields must be high enough to guarantee an effective purification. On the other hand, in cases in which the clariflocculation is used as a preliminary treatment phase, in a more complex chain that involves refining by successive processes (Verma *et al.* 2010), the law does not give particularly restrictive indications. Specifically, it is possible to accept lower efficiencies because the removal refinement will occur in the downstream units. Substantially, the most restrictive removal limits concern COD and TPH. Table 6 shows the impacts assigned to the different pollutants' removal ranges, referring to the two different scenarios analyzed.

In the case of TOC and turbidity, the law does not prescribe limits, so it was decided to assign optimal impact to efficiencies above 80% for TOC and above 90% for turbidity.

The following figures show the impacts associated with the removal performance of the various pollutant parameters that were obtained with the different process alternatives, i.e., with different types and doses of coagulant and flocculant, in both scenarios studied (treatment and pretreatment).

Table 6 | Impacts associated with different COD and TPH removal yields in the case of 'treatment' and 'pretreatment'

Treatment		**Pretreatment**	
Performance	**Impact**	**Performance**	**Impact**
COD			
<70%	Very bad	<30%	Very bad
70 ± 80%	Mediocre	30 ± 50%	Mediocre
80 ±90%	Satisfactory	50 ± 70%	Satisfactory
> 90%	Optimum	70 ± 80%	Optimum
TPH			
<50%	Very bad	<30%	Very bad
50 ± 80%	Mediocre	30 ± 50%	Mediocre
80 ± 90%	Well	50 ± 90%	Well
>90%	Optimum	>90%	Optimum

Figure 2(a) shows that for the COD there are no optimal impacts when the clarification is used as a 'treatment'. Satisfactory impacts occur only when aluminum sulfate is used as a coagulant, with the addition of substantial doses of flocculant. In this case, removal rates equal to 81.90% were obtained for $\text{ALS}_{50}\text{A57}_{10}$, equal to 84.01% for $\text{ALS}_{70}\text{A57}_{10}$, and equal to 84.00% for $\text{ALS}_{90}\text{A57}_{5}$. Otherwise, Figure 2(b) shows that when the process is used as a 'pretreatment', the impacts of different alternatives are excellent, always using aluminum sulfate as a coagulant and adding high doses of A57 as a flocculant. In these cases, removal efficiencies between 70 and 80% are defined as excellent since they allow a partial, but not total, removal that allows obtaining a totally purified wastewater following the subsequent biological treatment.

Looking at Figure 3(a) regarding the TPH removal in the case of 'treatment', there are no excellent or satisfactory performances with any of the different process alternatives. This behavior, as mentioned above, is due to the strong restriction of the law that requires particularly high removal rates. In the case in which, on the other hand, the clariflocculation is inserted as a 'pretreatment' within a more complex chain, there are instead good impacts for a high number of tests, as shown in Figure 3(b).

For the TOC (Figure 4) and the turbidity (Figure 5), as previously said, the law does not give precise indications, so it was decided to attribute the highest impact to the combinations that allow obtaining efficiencies higher than 80 and 90% respectively, regardless of the function of the clariflocculation within the treatment chain.

For these two pollution parameters, optimal impacts were obtained: for the TOC in all tests in which 70 mg L^{-1} of ferric chloride was used with the addition of the flocculant in any dose; while for the turbidity in the $\text{ALS}_{90}\text{A57}_{7.5}$ and $\text{ALS}_{90}\text{A57}_{10}$ tests with removal efficiencies of 94.72 and 92.96% respectively.

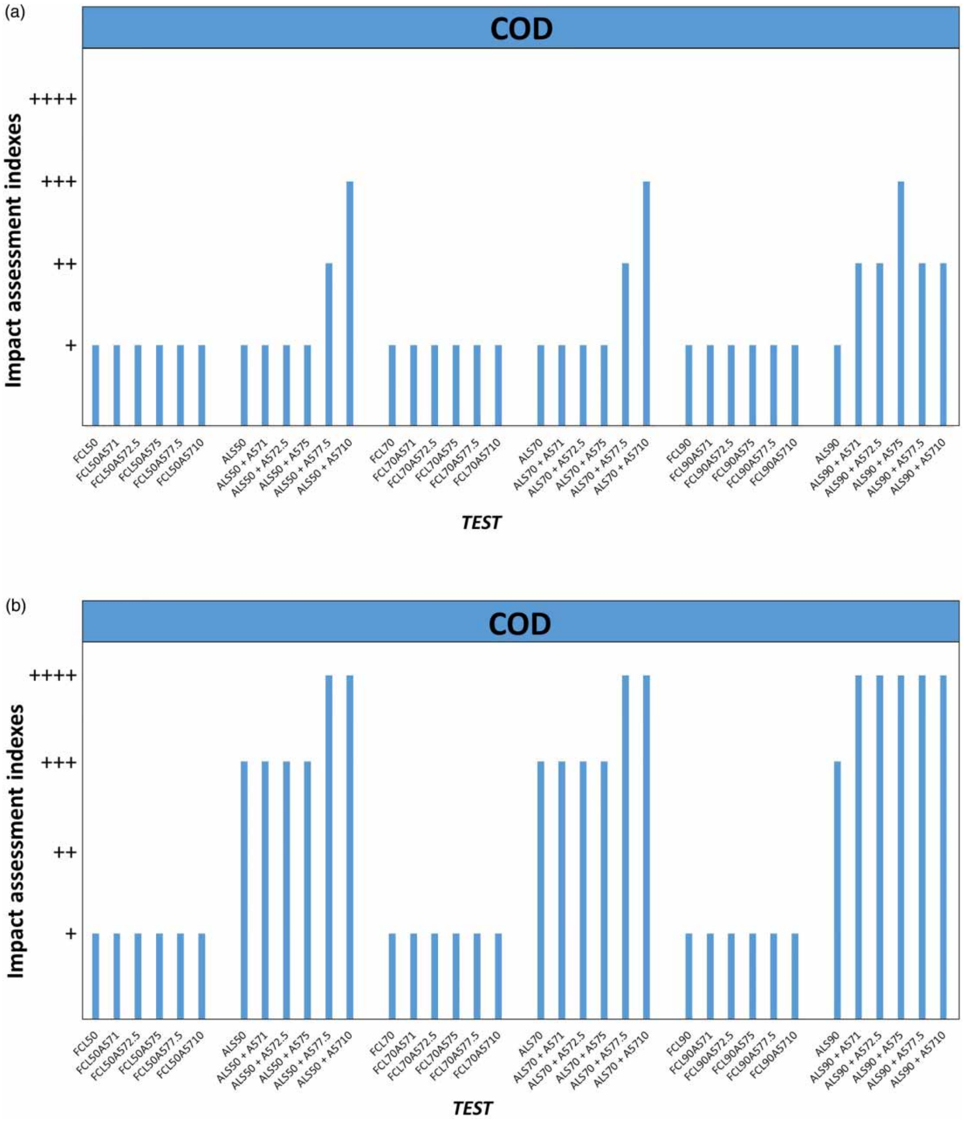


Figure 2 | Impact assessment indexes associated with the removal of COD in the case of treatment (a) and pretreatment (b).

Figure 6 shows that, with regard to monetary costs, in both scenarios studied (treatment and pretreatment), an optimal impact was assigned to tests in which no flocculant was used, while a worsening of the impact was observed as the added flocculant dose increases.

At this point, in order to identify the choices that allow a treatment optimization, two different contexts have been defined also based on the requests of the public administration:

- *Environmental scenario*, in which preferences are linked to alternatives that protect environmental objectives.
- *Economic scenario*, where the greatest attention is to monetary costs.

A preference was then given to each of the two scenarios as shown in Table 7. In the evaluation of the process within the environmental scenario, the greatest weight was attributed to COD and TPH, followed by the TOC and turbidity, while not high preferability was attributed to the total cost. The objective of these choices is to favor an environmental scenario to respect the limits imposed by Legislative Decree 152/06 for COD and TPH and to ensure high removal rates for TOC and turbidity, leaving aside the economic aspect. The same

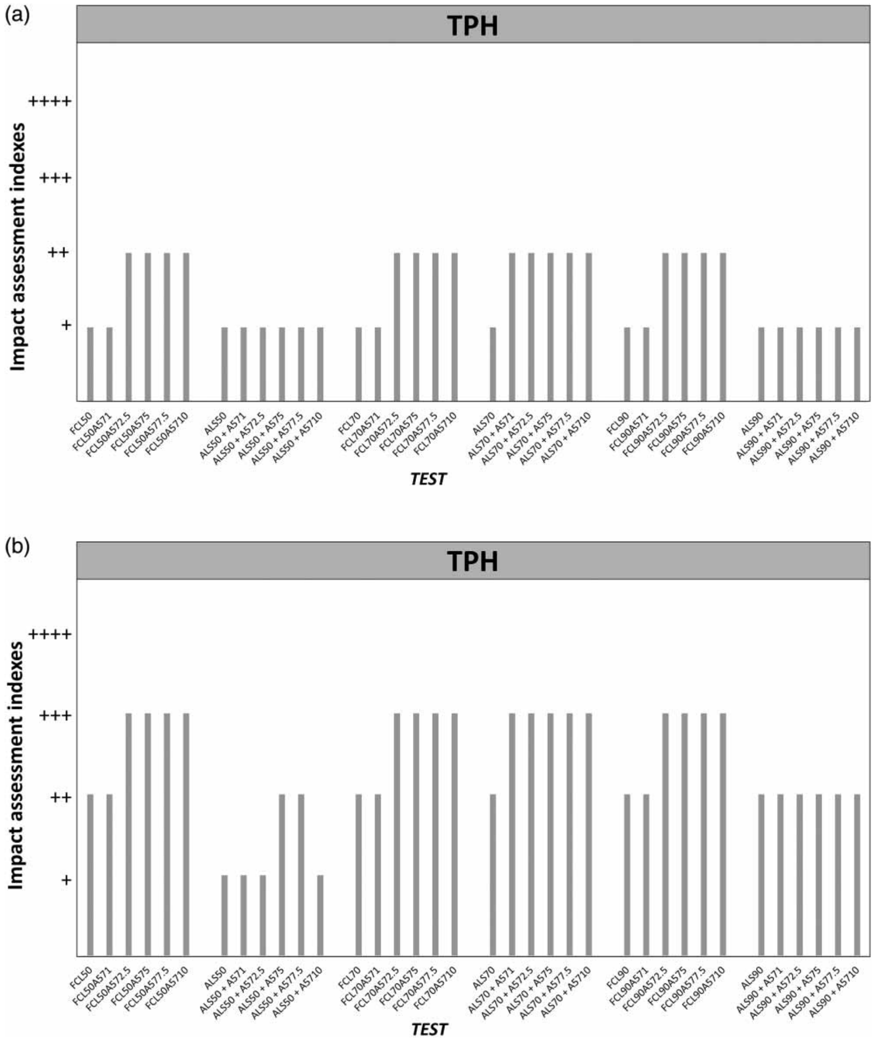


Figure 3 | Impact assessment indexes associated with the removal of TPH in the case of treatment (a) and pretreatment (b).

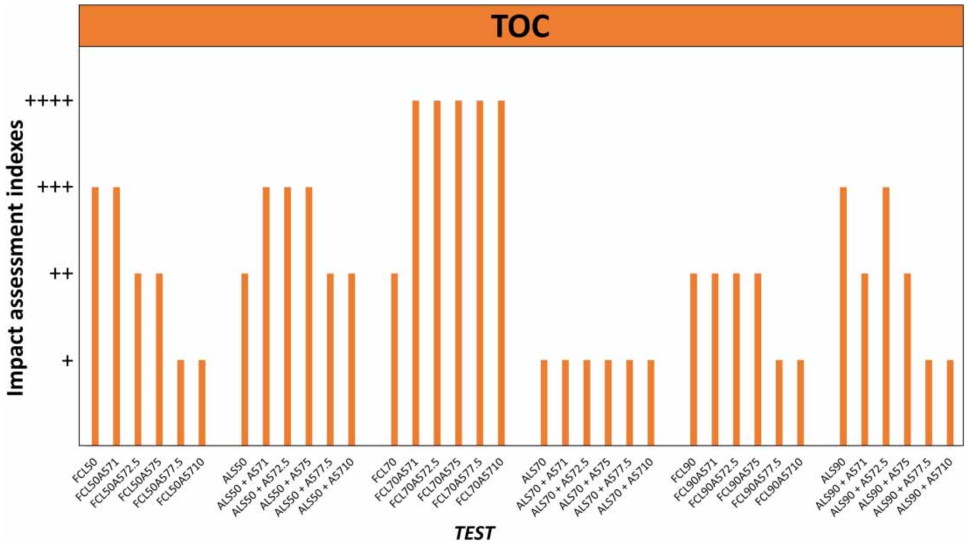


Figure 4 | Impact assessment indexes associated with the removal of TOC.

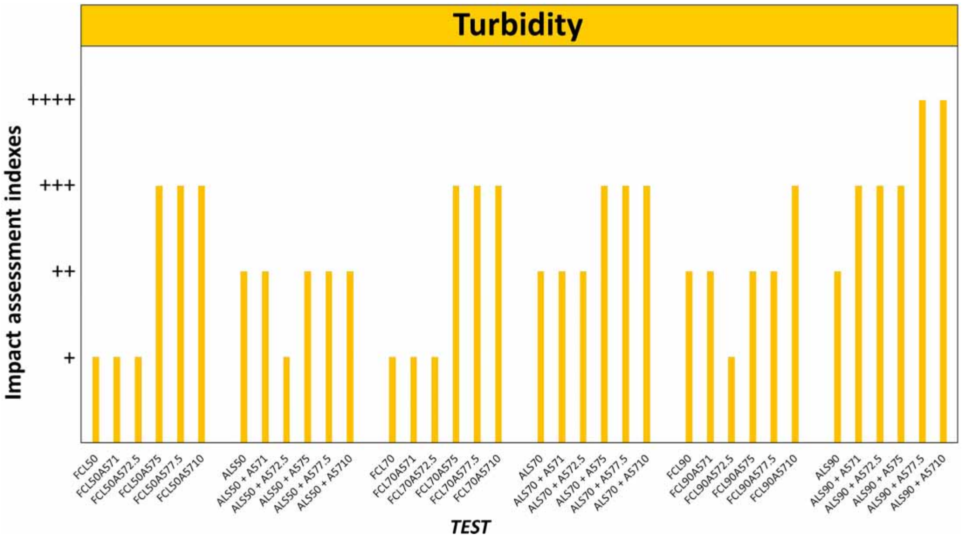


Figure 5 | Impact assessment indexes associated with the removal of turbidity.

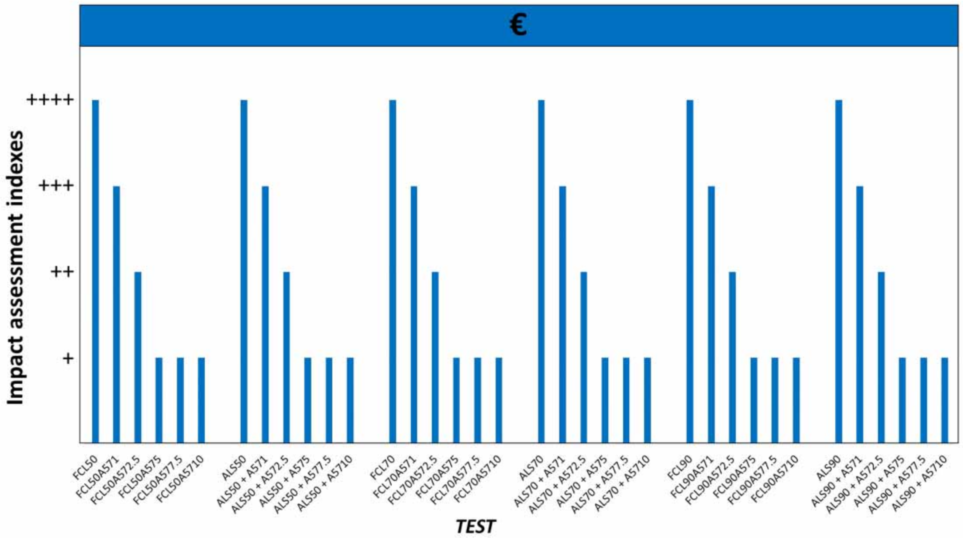


Figure 6 | Impact assessment indexes associated with the monetary costs.

Table 7 | Preferability assigned to the different criteria in both the analyzed scenarios

	COD	TOC	TPH	Turbidity	€
Scenario	**Preferability**				
Environmental	***	**	***	**	*
Economic	*	*	*	**	***

preferabilities have been assigned for both purposes using clariflocculation (treatment and pretreatment) where, as already observed, the impacts can vary.

Conversely, with reference to the economic scenario, it was decided to privilege the monetary aspect by assigning the greater preferability to total costs, average preferability to turbidity as this is removed with high efficiencies in all process alternatives, and not high preference to components strictly environmental (COD, TPH, and TOC). Once again, the same preferences were assigned both in the case of treatment and in that of pretreatment. Table 7 shows the preferences assigned to the different criteria in both the studied scenarios.

Table 8 | Frequency table for the 'treatment' environmental scenario

	***				**				*			
TEST	++++	+++	++	+	++++	+++	++	+	++++	+++	++	+
FCL_{50}	0	0	0	2	0	1	0	1	1	0	0	0
$FCL_{50}A57_{1}$	0	0	0	2	0	1	0	1	0	1	0	0
$FCL_{50}A57_{2.5}$	0	0	1	1	0	0	1	1	0	0	1	0
$FCL_{50}A57_{5}$	0	0	1	1	0	1	1	0	0	0	0	1
$FCL_{50}A57_{7.5}$	0	0	1	1	0	1	0	1	0	0	0	1
$FCL_{50}A57_{10}$	0	0	1	1	0	1	0	1	0	0	0	1
ALS_{50}	0	0	0	2	0	0	2	0	1	0	0	0
$ALS_{50}+A57_{1}$	0	0	0	2	0	1	1	0	0	1	0	0
$ALS_{50}+A57_{2.5}$	0	0	0	2	0	1	0	1	0	0	1	0
$ALS_{50}+A57_{5}$	0	0	0	2	0	1	1	0	0	0	0	1
$ALS_{50}+A57_{7.5}$	0	0	1	1	0	0	2	0	0	0	0	1
$ALS_{50}+A57_{10}$	0	1	0	1	0	0	2	0	0	0	0	1
FCL_{70}	0	0	0	2	0	0	1	1	1	0	0	0
$FCL_{70}A57_{1}$	0	0	0	2	1	0	0	1	0	1	0	0
$FCL_{70}A57_{2.5}$	0	0	1	1	1	0	0	1	0	0	1	0
$FCL_{70}A57_{5}$	0	0	1	1	1	1	0	0	0	0	0	1
$FCL_{70}A57_{7.5}$	0	0	1	1	1	1	0	0	0	0	0	1
$FCL_{70}A57_{10}$	0	0	1	1	1	1	0	0	0	0	0	1
ALS_{70}	0	0	0	2	0	0	1	1	1	0	0	0
$ALS_{70}+A57_{1}$	0	0	1	1	0	0	1	1	0	1	0	0
$ALS_{70}+A57_{2.5}$	0	0	1	1	0	0	1	1	0	0	1	0
$ALS_{70}+A57_{5}$	0	0	1	1	0	1	0	1	0	0	0	1
$ALS_{70}+A57_{7.5}$	0	0	2	0	0	1	0	1	0	0	0	1
$ALS_{70}+A57_{10}$	0	1	1	0	0	1	0	1	0	0	0	1
FCL_{90}	0	0	0	2	0	0	2	0	1	0	0	0
$FCL_{90}A57_{1}$	0	0	0	2	0	0	2	0	0	1	0	0
$FCL_{90}A57_{2.5}$	0	0	1	1	0	0	1	1	0	0	1	0
$FCL_{90}A57_{5}$	0	0	1	1	0	0	2	0	0	0	0	1
$FCL_{90}A57_{7.5}$	0	0	1	1	0	0	1	1	0	0	0	1
$FCL_{90}A57_{10}$	0	0	1	1	0	1	0	1	0	0	0	1
ALS_{90}	0	0	0	2	0	1	1	0	1	0	0	0
$ALS_{90}+A57_{1}$	0	0	1	1	0	1	1	0	0	1	0	0
$ALS_{90}+A57_{2.5}$	0	0	1	1	0	2	0	0	0	0	1	0
$ALS_{90}+A57_{5}$	0	1	0	1	0	1	1	0	0	0	0	1
$ALS_{90}+A57_{7.5}$	0	0	1	1	1	0	0	1	0	0	0	1
$ALS_{90}+A57_{10}$	0	0	1	1	1	0	0	1	0	0	0	1

Construction of the frequency table

In order to find the optimal alternative for the clariflocculation treatment that best suits each of the scenarios analyzed, for each analyzed case a 'frequency table' was built. In these tables, each number represents the 'frequency' with which a certain impact (of type ++++, +++, ++, +) occurs, with respect to an objective characterized by a certain degree of

Table 9 | Frequency table for the 'pretreatment' environmental scenario

	***				**				*			
TEST	++++	+++	++	+	++++	+++	++	+	++++	+++	++	+
FCL_{50}	0	0	1	1	0	1	0	1	1	0	0	0
$FCL_{50}A57_1$	0	0	1	1	0	1	0	1	0	1	0	0
$FCL_{50}A57_{2.5}$	0	1	0	1	0	0	1	1	0	0	1	0
$FCL_{50}A57_5$	0	1	0	1	0	1	1	0	0	0	0	1
$FCL_{50}A57_{7.5}$	0	1	0	1	0	1	0	1	0	0	0	1
$FCL_{50}A57_{10}$	0	1	0	1	0	1	0	1	0	0	0	1
ALS_{50}	0	1	0	1	0	0	2	0	1	0	0	0
$ALS_{50} + A57_1$	0	1	0	1	0	1	1	0	0	1	0	0
$ALS_{50} + A57_{2.5}$	0	1	0	1	0	1	0	1	0	0	1	0
$ALS_{50} + A57_5$	0	1	1	0	0	1	1	0	0	0	0	1
$ALS_{50} + A57_{7.5}$	1	0	1	0	0	0	2	0	0	0	0	1
$ALS_{50} + A57_{10}$	1	0	0	1	0	0	2	0	0	0	0	1
FCL_{70}	0	0	1	1	0	0	1	1	1	0	0	0
$FCL_{70}A57_1$	0	0	1	1	1	0	0	1	0	1	0	0
$FCL_{70}A57_{2.5}$	0	1	0	1	1	0	0	1	0	0	1	0
$FCL_{70}A57_5$	0	1	0	1	1	1	0	0	0	0	0	1
$FCL_{70}A57_{7.5}$	0	1	0	1	1	1	0	0	0	0	0	1
$FCL_{70}A57_{10}$	0	1	0	1	1	1	0	0	0	0	0	1
ALS_{70}	0	1	1	0	0	0	1	1	1	0	0	0
$ALS_{70} + A57_1$	0	2	0	0	0	0	1	1	0	1	0	0
$ALS_{70} + A57_{2.5}$	0	2	0	0	0	0	1	1	0	0	1	0
$ALS_{70} + A57_5$	0	2	0	0	0	1	0	1	0	0	0	1
$ALS_{70} + A57_{7.5}$	1	1	0	0	0	1	0	1	0	0	0	1
$ALS_{70} + A57_{10}$	1	1	0	0	0	1	0	1	0	0	0	1
FCL_{90}	0	0	1	1	0	0	2	0	1	0	0	0
$FCL_{90}A57_1$	0	0	1	1	0	0	2	0	0	1	0	0
$FCL_{90}A57_{2.5}$	0	1	0	1	0	0	1	1	0	0	1	0
$FCL_{90}A57_5$	0	1	0	1	0	0	2	0	0	0	0	1
$FCL_{90}A57_{7.5}$	0	1	0	1	0	0	1	1	0	0	0	1
$FCL_{90}A57_{10}$	0	1	0	1	0	1	0	1	0	0	0	1
ALS_{90}	0	1	1	0	0	1	1	0	1	0	0	0
$ALS_{90} + A57_1$	1	0	1	0	0	1	1	0	0	1	0	0
$ALS_{90} + A57_{2.5}$	1	0	1	0	0	2	0	0	0	0	1	0
$ALS_{90} + A57_5$	1	0	1	0	0	1	1	0	0	0	0	1
$ALS_{90} + A57_{7.5}$	1	0	1	0	1	0	0	1	0	0	0	1
$ALS_{90} + A57_{10}$	1	0	1	0	1	0	0	1	0	0	0	1

preferability or weight (of type ***, **, *). Tables 8 and 9 show the frequency tables for the two cases (treatment and pretreatment) related to the environmental scenario.

Likewise, Tables 10 and 11 show the frequency tables relating to the economic scenario respectively for the case of 'treatment' and 'pretreatment'.

Table 10 | Frequency table for the 'treatment' economic scenario

	***				**				*			
TEST	++++	+++	++	+	++++	+++	++	+	++++	+++	++	+
FCL$_{50}$	1	0	0	0	0	0	0	1	0	1	0	2
FCL$_{50}$A57$_{1}$	0	1	0	0	0	0	0	1	0	1	0	2
FCL$_{50}$A57$_{2.5}$	0	0	1	0	0	0	0	1	0	0	2	1
FCL$_{50}$A57$_{5}$	0	0	0	1	0	1	0	0	0	0	2	1
FCL$_{50}$A57$_{7.5}$	0	0	0	1	0	1	0	0	0	0	1	2
FCL$_{50}$A57$_{10}$	0	0	0	1	0	1	0	0	0	0	1	2
ALS$_{50}$	1	0	0	0	0	0	1	0	0	0	1	2
ALS$_{50}$ + A57$_{1}$	0	1	0	0	0	0	1	0	0	1	0	2
ALS$_{50}$ + A57$_{2.5}$	0	0	1	0	0	0	0	1	0	1	0	2
ALS$_{50}$ + A57$_{5}$	0	0	0	1	0	0	1	0	0	1	0	2
ALS$_{50}$ + A57$_{7.5}$	0	0	0	1	0	0	1	0	0	0	2	1
ALS$_{50}$ + A57$_{10}$	0	0	0	1	0	0	1	0	0	1	1	1
FCL$_{70}$	1	0	0	0	0	0	0	1	0	0	1	2
FCL$_{70}$A57$_{1}$	0	1	0	0	0	0	0	1	1	0	0	2
FCL$_{70}$A57$_{2.5}$	0	0	1	0	0	0	0	1	1	0	1	1
FCL$_{70}$A57$_{5}$	0	0	0	1	0	1	0	0	1	0	1	1
FCL$_{70}$A57$_{7.5}$	0	0	0	1	0	1	0	0	1	0	1	1
FCL$_{70}$A57$_{10}$	0	0	0	1	0	1	0	0	1	0	1	1
ALS$_{70}$	1	0	0	0	0	0	1	0	0	0	0	3
ALS$_{70}$ + A57$_{1}$	0	1	0	0	0	0	1	0	0	0	1	2
ALS$_{70}$ + A57$_{2.5}$	0	0	1	0	0	0	1	0	0	0	1	2
ALS$_{70}$ + A57$_{5}$	0	0	0	1	0	1	0	0	0	0	1	2
ALS$_{70}$ + A57$_{7.5}$	0	0	0	1	0	1	0	0	0	0	2	1
ALS$_{70}$ + A57$_{10}$	0	0	0	1	0	1	0	0	0	1	1	1
FCL$_{90}$	1	0	0	0	0	0	1	0	0	0	1	2
FCL$_{90}$A57$_{1}$	0	1	0	0	0	0	1	0	0	0	1	2
FCL$_{90}$A57$_{2.5}$	0	0	1	0	0	0	0	1	0	0	2	1
FCL$_{90}$A57$_{5}$	0	0	0	1	0	0	1	0	0	0	2	1
FCL$_{90}$A57$_{7.5}$	0	0	0	1	0	0	1	0	0	0	1	2
FCL$_{90}$A57$_{10}$	0	0	0	1	0	1	0	0	0	0	1	2
ALS$_{90}$	1	0	0	0	0	0	1	0	0	1	0	2
ALS$_{90}$ + A57$_{1}$	0	1	0	0	0	1	0	0	0	0	2	1
ALS$_{90}$ + A57$_{2.5}$	0	0	1	0	0	1	0	0	0	1	1	1
ALS$_{90}$ + A57$_{5}$	0	0	0	1	0	1	0	0	0	1	1	1
ALS$_{90}$ + A57$_{7.5}$	0	0	0	1	1	0	0	0	0	0	1	2
ALS$_{90}$ + A57$_{10}$	0	0	0	1	1	0	0	0	0	0	1	2

The alternatives were sorted according to an order of preference of the treatments based on an ordered scale of values attributed to the binomial 'criterion + impact' as shown in Table 12.

The comparison between the treatment alternatives is carried out considering the sum of the binomial values for the two cases analyzed (treatment and pretreatment). This comparison is carried out with the aim of identifying

Table 11 | Frequency table for the 'pretreatment' economic scenario

	***				**				*			
TEST	++++	+++	++	+	++++	+++	++	+	++++	+++	++	+
FCL$_{50}$	1	0	0	0	0	0	0	1	0	1	1	1
FCL$_{50}$A57$_{1}$	0	1	0	0	0	0	0	1	0	1	1	1
FCL$_{50}$A57$_{2.5}$	0	0	1	0	0	0	0	1	0	1	1	1
FCL$_{50}$A57$_{5}$	0	0	0	1	0	1	0	0	0	1	1	1
FCL$_{50}$A57$_{7.5}$	0	0	0	1	0	1	0	0	0	1	0	2
FCL$_{50}$A57$_{10}$	0	0	0	1	0	1	0	0	0	1	0	2
ALS$_{50}$	1	0	0	0	0	0	1	0	0	1	1	1
ALS$_{50}$ + A57$_{1}$	0	1	0	0	0	0	1	0	0	2	0	1
ALS$_{50}$ + A57$_{2.5}$	0	0	1	0	0	0	0	1	0	2	0	1
ALS$_{50}$ + A57$_{5}$	0	0	0	1	0	0	1	0	0	2	1	0
ALS$_{50}$ + A57$_{7.5}$	0	0	0	1	0	0	1	0	1	1	2	0
ALS$_{50}$ + +A57$_{10}$	0	0	0	1	0	0	1	0	1	1	1	1
FCL$_{70}$	1	0	0	0	0	0	0	1	0	0	2	1
FCL$_{70}$A57$_{1}$	0	1	0	0	0	0	0	1	1	0	1	1
FCL$_{70}$A57$_{2.5}$	0	0	1	0	0	0	0	1	1	1	0	1
FCL$_{70}$A57$_{5}$	0	0	0	1	0	1	0	0	1	1	0	1
FCL$_{70}$A57$_{7.5}$	0	0	0	1	0	1	0	0	1	1	0	1
FCL$_{70}$A57$_{10}$	0	0	0	1	0	1	0	0	1	1	0	1
ALS$_{70}$	1	0	0	0	0	0	1	0	0	1	1	1
ALS$_{70}$ + A57$_{1}$	0	1	0	0	0	0	1	0	0	2	0	1
ALS$_{70}$ + A57$_{2.5}$	0	0	1	0	0	0	1	0	0	2	0	1
ALS$_{70}$ + A57$_{5}$	0	0	0	1	0	1	0	0	0	2	0	1
ALS$_{70}$ + A57$_{7.5}$	0	0	0	1	0	1	0	0	1	1	0	1
ALS$_{70}$ + A57$_{10}$	0	0	0	1	0	1	0	0	1	1	0	1
FCL$_{90}$	1	0	0	0	0	0	1	0	0	0	2	1
FCL$_{90}$A57$_{1}$	0	1	0	0	0	0	1	0	0	0	2	1
FCL$_{90}$A57$_{2.5}$	0	0	1	0	0	0	0	1	0	1	1	1
FCL$_{90}$A57$_{5}$	0	0	0	1	0	0	1	0	0	1	1	1
FCL$_{90}$A57$_{7.5}$	0	0	0	1	0	0	1	0	0	1	0	2
FCL$_{90}$A57$_{10}$	0	0	0	1	0	1	0	0	0	1	0	2
ALS$_{90}$	1	0	0	0	0	0	1	0	0	2	1	0
ALS$_{90}$ + A57$_{1}$	0	1	0	0	0	1	0	0	1	0	2	0
ALS$_{90}$ + A57$_{2.5}$	0	0	1	0	0	1	0	0	1	1	1	0
ALS$_{90}$ + A57$_{5}$	0	0	0	1	0	1	0	0	1	0	2	0
ALS$_{90}$ + A57$_{7.5}$	0	0	0	1	1	0	0	0	1	0	1	1
ALS$_{90}$ + A57$_{10}$	0	0	0	1	1	0	0	0	1	0	1	1

possible Pareto dominances (and this would cause the elimination of the dominated alternative) or to evaluate the relative dominances among the remaining alternatives. It was therefore possible to assign a final score to each analyzed design alternative, as shown in Table 13 where the values for the environmental and economic scenarios are reported. This score is obtained from the product of the value attributed to the binomial 'criterion + impact' and the frequency of each impact reported in the frequency tables.

For the environmental scenario, the maximum score awarded is 47 for ALS_{90}, $ALS_{90}A57_1$, and $ALS_{90}A57_{2.5}$. These alternatives have the maximum value, equal to 41, also for the analysis carried out considering the economic scenario. To choose the optimal alternative it was therefore appropriate to compare the removal efficiencies (Table 14). From this analysis, the alternative $ALS_{90}A57_1$ was eliminated as the removal performance of TPH (equal to 38.79%) is not adequate to reach pollutant output values that respect the limits imposed by current legislation. The remaining two alternatives, on the other hand, are adequate as they guarantee high removal efficiencies of the pollutants considered, as reported in Table 14.

As Table 13 shows, other alternatives deserve attention as they report scores of 45 and 44 for the environmental scenario near the maximum value. In particular, the value 45 was obtained from the process alternatives in which 70 mg L^{-1} of ferric chloride was used with different doses of flocculant. However, these alternatives are not considered optimal due to the rather low COD removal rate,

Table 12 | Values attributed to the binomial 'criterion + impact'

Criterion + Impact	Value
++ ++***	7
++++**	6
+++***	6
++++*	5
+++**	5
++ ***	5
+++ *	4
++ **	4
+***	4
++ *	3
+**	3
+*	2

Table 14 | Removal efficiencies for optimal process alternatives

Alternative	ηCOD	ηTPH	ηTOC	ηTurbidity
ALS_{90}	58.85	47.78	72.71	77.08
$ALS_{90}A57_{2.5}$	77.73	40.52	77.31	87.60

Table 13 | Final score attributed to each process alternative for the environmental and economic scenarios

TEST	Environmental scenario	Economic scenario	TEST	Environmental scenario	Economic scenario
FCL_{50}	43	37	ALS_{50}	44	38
$FCL_{50}A57_1$	41	35	$ALS_{50} + A57_1$	44	38
$FCL_{50}A57_{2.5}$	39	33	$ALS_{50} + A57_{2.5}$	40	34
$FCL_{50}A57_5$	41	35	$ALS_{50} + A57_5$	41	35
$FCL_{50}A57_{7.5}$	39	33	$ALS_{50} + A57_{7.5}$	41	35
$FCL_{50}A57_{10}$	39	33	$ALS_{50} + A57_{10}$	41	35
FCL_{70}	41	35	ALS_{70}	43	37
$FCL_{70}A57_1$	43	37	$ALS_{70} + A57_1$	43	37
$FCL_{70}A57_{2.5}$	43	37	$ALS_{70} + A57_{2.5}$	41	35
$FCL_{70}A57_5$	45	39	$ALS_{70} + A57_5$	41	35
$FCL_{70}A57_{7.5}$	45	39	$ALS_{70} + A57_{7.5}$	43	37
$FCL_{70}A57_{10}$	45	39	$ALS_{70} + A57_{10}$	44	38
FCL_{90}	43	37	ALS_{90}	47	41
$FCL_{90}A57_1$	41	35	$ALS_{90} + A57_1$	47	41
$FCL_{90}A57_{2.5}$	39	33	$ALS_{90} + A57_{2.5}$	47	41
$FCL_{90}A57_5$	39	33	$ALS_{90} + A57_5$	44	38
$FCL_{90}A57_{7.5}$	37	31	$ALS_{90} + A57_{7.5}$	43	37
$FCL_{90}A57_{10}$	39	33	$ALS_{90} + A57_{10}$	43	37

which is always around 20%. The score 44 was instead obtained with different doses of aluminum sulfate; in this case the removal yields respect the values imposed by the law for all the pollutants considered, but overall, they are not optimal if compared with those of the alternatives with a score of 47. Moreover, for the economic scenario, there are other alternatives to take into account since they obtained values of 39 and close to the maximum value. However, in these process alternatives, ferric chloride was used as a coagulant, which has a much higher total cost than aluminum sulfate and, for this reason, it has been eliminated. Therefore, in general, the preferred alternatives are ALS_{90} and $ALS_{90}A57_{2.5}$.

CONCLUSIONS

The present study compares the different process alternatives available for the clariflocculation treatment able to remove pollutants from salt wastewater contaminated with hydrocarbons. Basically, this comparison was performed both from an environmental point of view, considering the discharge limits imposed by the law, and from an economic point of view, considering the costs of the chemical reagents to be dosed during the process, trying to determine the optimal alternative that represents a fair compromise between the results obtained for the two scenarios.

In order to choose the best process alternative, a frequency analysis method belonging to the family of multi-criteria analyses was applied.

From the application of this method among the 36 design alternatives analyzed using jar tests, it emerged that as a coagulating agent, aluminum sulfate is preferable to ferric chloride and that the optimal dose is equal to 90 mg L^{-1}. The addition of the flocculant agent, on the other hand, leads to an excessive increase in the total treatment costs that cannot be justified by the reduced improvement in the pollutants' removal efficiency. Therefore, it is appropriate to avoid the use of anionic polyelectrolyte, or limit the doses to values not exceeding 2.5 mg L^{-1}, since the addition of the flocculant leads to a slight increase in the removal efficiency of some of the main polluting parameters.

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First received 22 January 2020; accepted in revised form 6 April 2020. Available online 23 April 2020